

## High Rate PLD of Diamond-Like-Carbon Utilizing High Repetition Rate Visible Lasers

William McLean II  
Edward J. Fehring  
Ernest P. Dragon  
Bruce E. Warner

This paper was prepared for submittal to the  
LaserTech '94  
Photonics Technology Transfer Conference  
Washington, DC  
November 9, 1994

September 15, 1994



Lawrence  
Livermore  
National  
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

#### DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

# **HIGH RATE PLD OF DIAMOND-LIKE-CARBON UTILIZING HIGH REPETITION RATE VISIBLE LASERS**

**William McLean II, Edward Fehring, Ernest Dragon, Bruce Warner**

**University of California  
Lawrence Livermore National Laboratory  
P. O. Box 808, L-466  
Livermore, CA 94551  
Tel: 510-422-9237 Fax: 510-423-7651**

## **ABSTRACT**

Pulsed Laser Deposition (PLD) has been shown to be an effective method for producing a wide variety of thin films of high-value-added materials. The high average powers and high pulse repetition frequencies of lasers under development at LLNL make it possible to scale-up PLD processes that have been demonstrated in small systems in a number of university, government, and private laboratories to industrially meaningful, economically feasible technologies. A copper vapor laser system at LLNL, operated at higher pulse repetition frequencies than are available with most commercial excimer or Nd:YAG systems, has been utilized to demonstrate high rate PLD of high quality diamond-like-carbon (DLC) from graphite targets. The deposition rates for PLD obtained with a 100 W laser were  $\approx 2000 \mu\text{m} \cdot \text{cm}^2/\text{h}$ , or roughly 100 times larger than those reported by chemical vapor deposition (CVD) or physical vapor deposition (PVD) methods. Good adhesion of thin (up to 1.5  $\mu\text{m}$ ) films has been achieved on a small number of substrates that include  $\text{SiO}_2$  and single crystal Si. Present results indicate that the best quality DLC films can be produced at optimum rates at power levels and wavelengths compatible with fiber optic delivery systems. If this is also true of other desirable coating systems, this PLD technology could become an extremely attractive industrial tool for high value added coatings.

## **INTRODUCTION**

Many high-value coatings have been produced by PLD. One of the distinct advantages of the PLD process is the near stoichiometric transfer from the ablation target to the desired substrate, a feature that is often difficult to achieve with conventional coating technologies such as magnetron sputtering or electron beam evaporation. In many cases, minor adjustments to the substrate temperature and/or background pressure of reactive gases result in adherent coatings with acceptable morphologies, correct stoichiometries, and desirable physical properties. Table 1 serves as an indication of potential thin-film systems and their applications.

Table 1. Materials with difficult stoichiometries that have been successfully coated by PLD.

Material	Laser	Use
BaFe <sub>12</sub> O <sub>19</sub>	KrF	High density hard disk coatings
BaTiO <sub>3</sub>	Nd:YAG	Optical coatings
Cubic BN	KrF	High temperature, radiation resistant semiconductors
Amorphous C	Nd:YAG XeCl	Cutting tool coatings
		Tribological coatings
		Heat sinks
		Field emitters for FPD's
Cd <sub>x</sub> Z <sub>1-x</sub> Te	KrF	Ir detectors
CoSi <sub>2</sub>	KrF	Low resistivity interconnects for fast switching Schottky rectifiers
MoS <sub>2</sub>	XeCl	High resistivity lubricating coating
NbSe <sub>2</sub>	KrF	Low resistivity lubricating coating
Pb(Zr <sub>0.54</sub> Ti <sub>0.46</sub> )O <sub>3</sub>	ArF	Piezoelectric devices
	Nd:YAG	Non volatile memory
SiC	XeF	High temperature, wide band gap semiconductors
TiO <sub>2</sub>	KrF	Antireflection coatings
YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	ArF, KrF	High T <sub>c</sub> superconductors
ZnO	KrF	Piezoelectric devices
	Nd:YAG(2x)	Phosphors

The majority of PLD studies utilize short wavelength (193 nm [ArF] to 308 nm [XeCl]) light arriving in 20–50 ns pulses with peak irradiances of 10<sup>8</sup>–10<sup>10</sup> W/cm<sup>2</sup> at rates of 5–30 Hz.<sup>1–6</sup> However, some authors report positive results with green (532 nm [frequency doubled Nd:YAG]) radiation sources operated under similar conditions.<sup>7</sup> Typical film formation rates for low pulse repetition frequency (PRF) systems are on the order of 10 μm-cm<sup>2</sup>/hr.<sup>1–6</sup>

The main impediments to large scale commercialization are the high cost, low power, and low pulse repetition rates of readily available laser systems. Our original experiments in deposition of DLC were guided by information gathered in the literature and by colleagues in the field of PLD. Conventional wisdom based on CO<sub>2</sub>, Nd:YAG and excimer laser experiments indicates deposition of DLC is most successful (in terms of film quality) when the target is irradiated with ultraviolet light.<sup>8</sup> The higher the photon energy, the higher the diamond like content of the coating. Murray,<sup>8</sup> has measured the population of ions of carbon polymers in the ablation plume with a time-of-flight mass spectrometer and has concluded that 193 nm generated plasmas have predominantly C<sup>+</sup> ions, where as the 1064 nm generated plasmas have predominantly C<sub>11</sub><sup>+</sup> – C<sub>13</sub><sup>+</sup> ion content. Other researchers claim that both Nd:YAG and CO<sub>2</sub> lasers can produce good material if the irradiance is 10<sup>10</sup> W/cm<sup>2</sup> or higher.<sup>3a</sup> These findings are phenomenologically explained by a dominant atomic carbon plasma of high kinetic energy created by laser absorption directly into the carbon plume.

## EXPERIMENTAL ARRANGMENT

A single copper vapor laser (CVL) oscillator and one high power amplifier were used for these studies. Nominal operating parameters are summarized in Table 2. The optical delivery system was comprised of a discrete optics delivery system and a single 500 mm focusing lens located

Table 2. Operating Parameters.

Wavelength:	510,578 nm (2:1)
Spot size on target:	50–300 $\mu\text{m}$
Irradiance	$2 \times 10^{10} - 4 \times 10^8 \text{ W/cm}^2$
Pulse repetition frequency:	4.4 kHz
Pulse width:	50 ns (FWHM)
Target speed:	8 cm/s
Target - Substrate Distance:	7.6 cm
DLC deposition rate:	$5.6 \times 10^{-2} \text{ \AA/pulse}$ at $4 \times 10^8 \text{ W/cm}^2$ $1.0 \times 10^{-3} \text{ \AA/pulse}$ at $2 \times 10^{10} \text{ W/cm}^2$

adjacent to the vacuum deposition tank. Relatively low irradiance ( $10^8 \text{ W/cm}^2$ ) on the target was necessary to achieve high deposition rates and good materials properties. This was accommodated by defocusing the beam on the target.

A schematic drawing of the deposition chamber is shown in Fig. 1. The laser light is introduced through a fused silica window. The graphite target is a rod of 2.5 cm diameter that is mechanically rotated at approximately 1 RPS and can be manually moved axially to keep a relatively fresh surface. The laser is aligned to strike the rod off center so that the laser plume is at 45 or 60 degrees to the incident beam. In general, the ablation plumes expand normal to the surface. The substrate to be coated is mounted within a sample port that is easily removed for deposition on multiple substrates. The graphite target to substrate distance is 7.6 cm. Viewports orthogonal to the laser and plume and in the scattered laser direction were used to help diagnose laser alignment, plume generation, and qualitatively assess macroparticle generation.

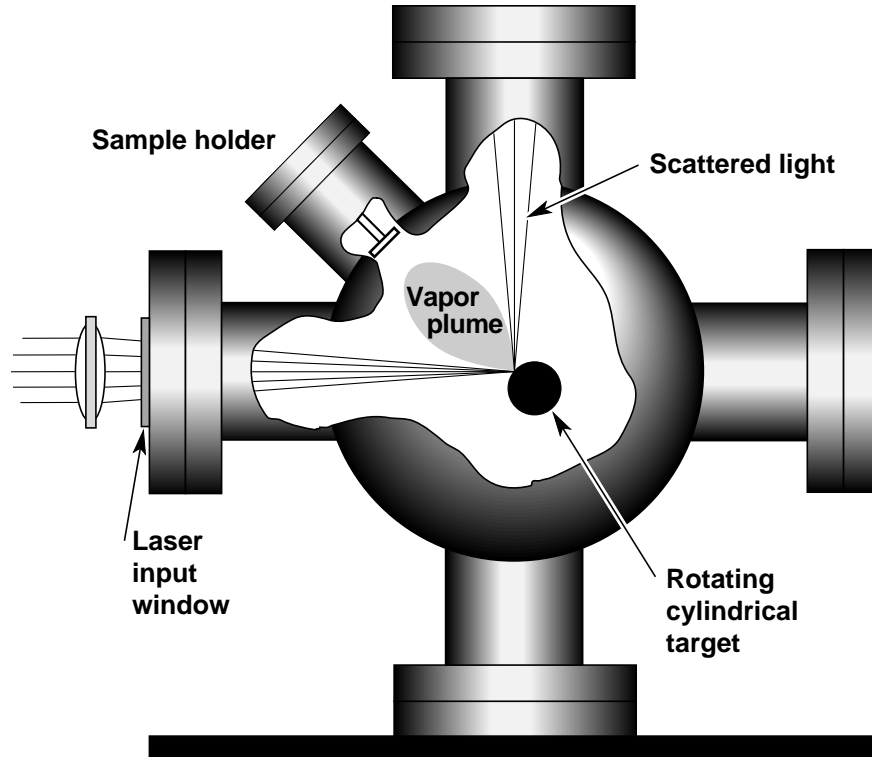


Figure 1. Developmental PLD chamber schematic.

A turbomolecular pump was used to achieve a base pressure of  $5 \times 10^{-8}$  Torr. For each set of deposition runs the vacuum chamber was heated up and outgassed. Typical vacuum levels during used. Several different substrates have been coated with DLC. However, consistent with results of others, adherence of the films are substrate dependent.

## DEPOSITION RESULTS

Our early experiments investigated the deposition of DLC at laser irradiance of  $10^8$  W/cm<sup>2</sup> to  $10^{10}$  W/cm<sup>2</sup>. Figure 2a and 2b are Elastic Electron Loss Spectroscopy (EELS) spectra performed on the resultant material (a) and on a graphite substrate (b). Typically there are three predominant features in an EELS DLC spectra. The elastic electron scattering peak is at the incident electron energy of 492 eV. There is a peak ~6.6 eV below the incident energy which represents energy lost to the  $\pi$ -bonds of graphite (at 485 eV in Fig. 2). The third feature is an unresolved, broad plasmon loss peak 30 to 40 eV below the incident energy. The DLC represented in Fig. 2a was deposited on a polished Si (100) substrate at a laser irradiance of  $3 \times 10^8$  W/cm<sup>2</sup>. Note the lack of a  $\pi$ - $\pi^*$  feature as compared to the graphite spectra in Fig. 2b. This material's spectra is similar to that of material produced by Murray with 193 nm wavelength light. Researchers in the field have also used Raman scattering off of the DLC films to help quantify its bond structure.<sup>9</sup> Figure 3 is a representative Raman spectra of our DLC film grown with the above parameters. This spectra verifies the DLC nature of the film.

The (silicon) substrates were masked while both the target irradiance and number of laser pulses were controlled to quantify the volume of DLC grown on the substrates. Its spatial distribution and its growth rate were determined by measuring film thickness and distribution with a diamond stylus profilometer at the step-up provided by the masked area. Figure 4 displays a measured DLC deposition thickness across the substrate. The deposition has a very peaked character typical of PLD. By offsetting the plume peak and spinning the substrate, we have been able to grow uniform DLC over 2 cm diameters. We believe a combination of scanned targets and manipulated substrates will allow uniform film growth over square meters.

The deposition profile in Fig. 4 has been fit with a plume distribution proportional to  $\cos^{10.5} \phi$  ( $\phi$  is the angle measured from the target surface normal). After  $10^5$  laser pulses at  $4 \times 10^8$  W/cm<sup>2</sup> (190 W average power), we achieved 410 nm thickness at the center with half thickness at a radius of ~4 cm. Since the copper lasers operate at 4.4 kHz,  $10^5$  pulses represents 23 seconds of elapsed time. Integrating the full volume of material and dividing by the elapsed time yields an average deposition rate of  $2 \times 10^3$   $\mu\text{m-cm}^2/\text{hr}$ . We have subsequently operated at 100 W average power at slightly lower target irradiance and have achieved  $2.6 \times 10^3$   $\mu\text{m-cm}^2/\text{hr}$ . At this rate we produce DLC coatings in minutes that would normally take hours by either low repetition rate lasers or RF plasma deposition (note that materials can have significantly different properties [such as hydrogen content] with RF plasma deposition). We have recently produced a 1.5  $\mu\text{m}$  thick DLC film on a silicon substrate, with good surface characteristics. This film was grown with 58 seconds of laser on time.

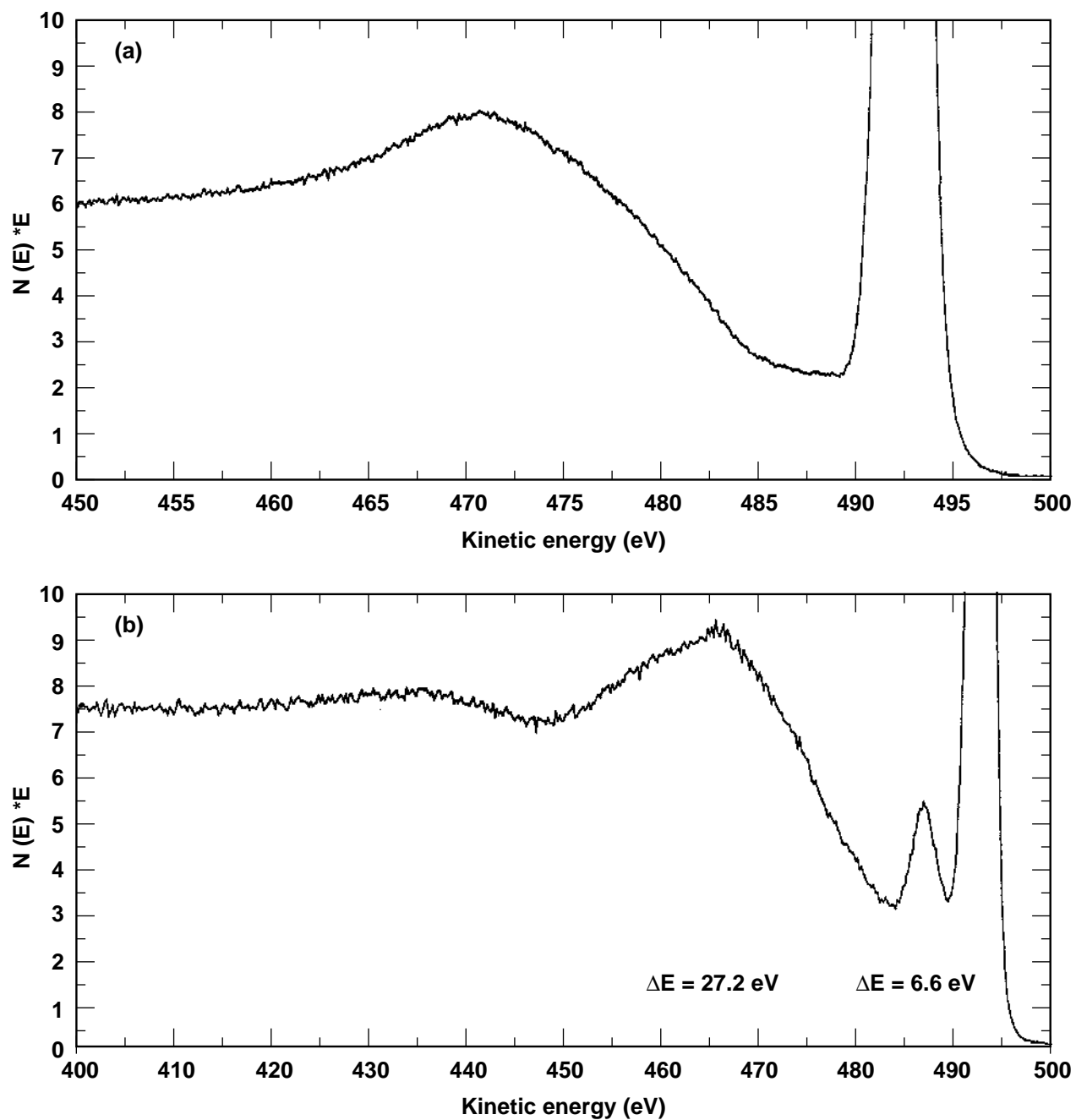


Figure 2. (a) EELS spectra of DLC produced at  $3 \times 10^8 \text{ W/cm}^2$ . (b) EELS spectra of graphite.

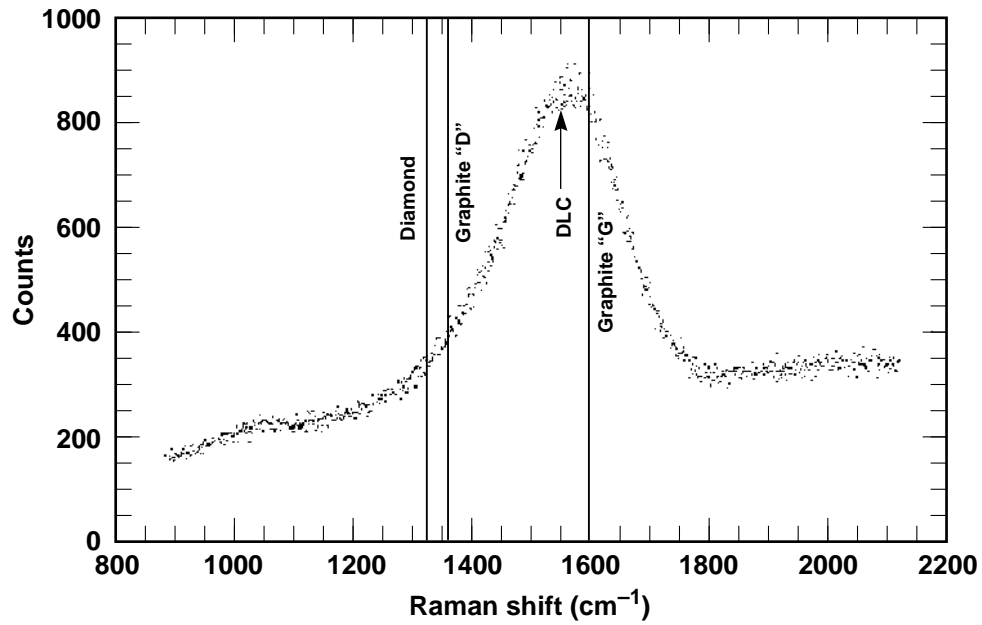


Figure 3. Raman spectrum of DLC film.

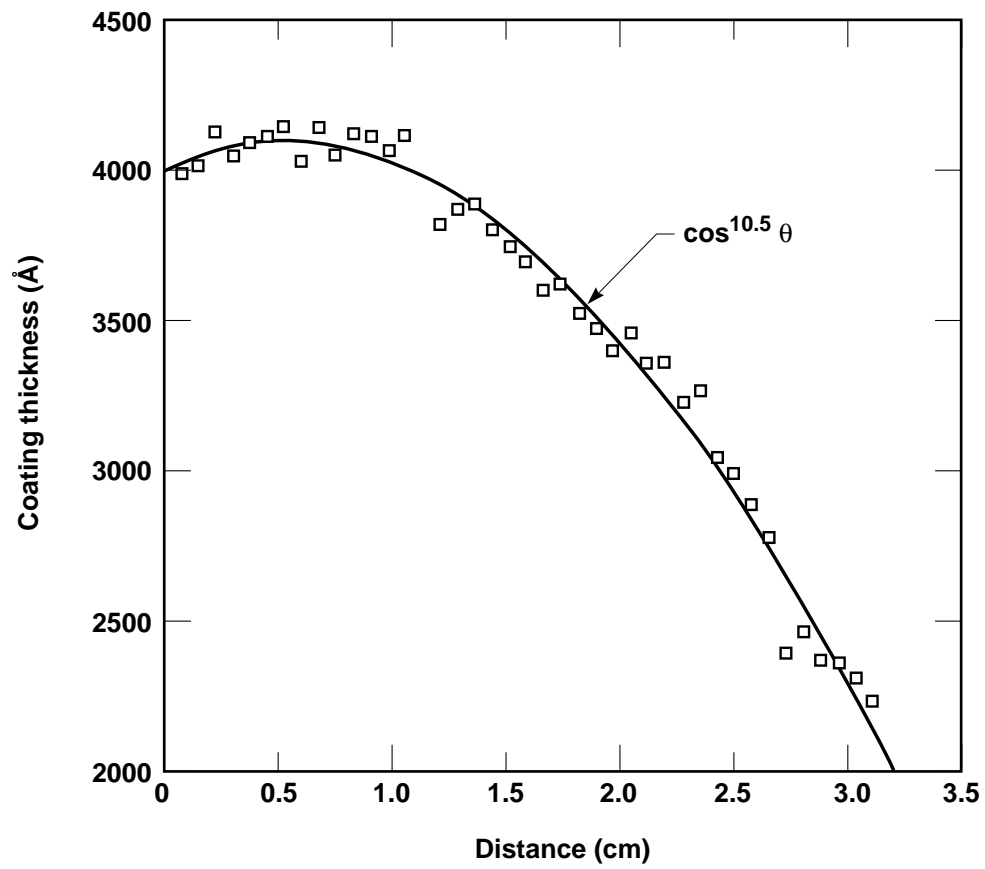


Figure 4. Typical PLD deposition profile.

Atomic Force Microscopy (AFM) was used to measure surface roughness. Figure 5 displays an AFM image of the DLC surface. The area depicted in the image is 0.5 by 0.5  $\mu\text{m}$ . Note that the vertical scale is 20 nm per division. This 400 nm thick DLC film has a surface roughness (as measured by the AFM) of  $\leq 10$  nm. We have produced some films with RMS surface roughness as low as a few nanometers.

Tool steel and tungsten carbide were coated as a demonstration of potential value to the machine tool and industrial processing industry. In our two attempts to coat the tool steel we have not been able to achieve good adherence. This has been observed by others.<sup>10</sup> The adhesion to steels seems to be related to the degree of saturation of the 4d or 5d bonds in the substrate material.<sup>11</sup> Steels with high carbon content (and metal carbides) are less likely to form carbides with the newly deposited carbon and, therefore, are better substrates for diamond formation. The DLC we deposited on a tungsten carbide tool bit survived the scotch tape test. The tool bit was subsequently sent out for further analysis. In the areas of the bit that were smooth enough to perform scratch tests upon, the DLC had excellent adherence.

## DISCUSSION

There are three observations we have made that add to the base of knowledge of PLD. First, visible light under our operating conditions appears to produce DLC with characteristics as good as material produced with ultraviolet sources. If these results hold with further investigation, it could greatly simplify large scale PLD equipment. Either copper vapor or Q-switched and doubled Nd:YAG lasers operated at high repetition rate should be much more readily incorporated into a thin film production line than ultraviolet sources. Visible light is easily delivered through optical fibers at high enough radiances to be used in PLD.

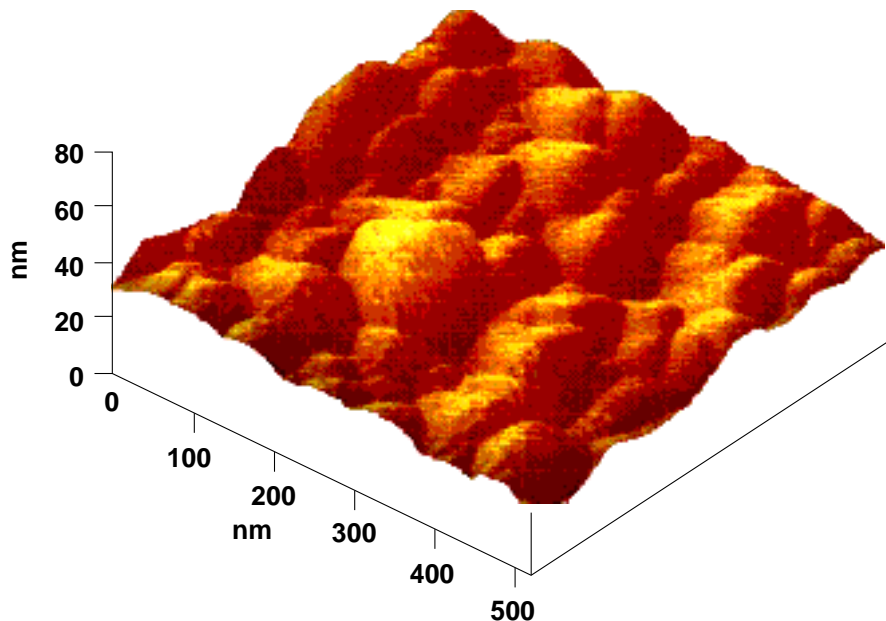


Figure 5. Atomic force microscope image of LLNL produced DLC surface.

The second observation we have made also appears important for PLD. The deposition rate of DLC scales with pulse repetition rate (at least to 4.4 kHz). This appears obvious, and in fact, is largely what motivated us in the first place to try PLD with the copper vapor lasers.

The third observation we have made is an improved surface character in our deposition tests. While this observation is semi-quantitative for the moment, our deposition regime is significantly different because of lower pulse energies (23 mJ versus 0.5 to 2 J) and higher repetition rates (4.4 kHz versus 10 to 20 Hz). We have found that we can produce good looking material as long as we have no more than 10 to 20 laser pulses on the same spot on the target. Based on our observations and modeling<sup>12</sup>, this should be no more than 2 to 3  $\mu\text{m}$  in depth in the graphite. We believe, as others, that much deeper target penetration leads to explosive removal of macroparticles, particularly around the spot periphery.

## **ENGINEERING ISSUES FOR HIGH RATE PLD HARDWARE**

Several potential issues associated with a high rate PLD system have been encountered in our small system. One issue is protection of the laser window from coating by the ablated material. We have found that commercially available 2.5  $\mu\text{m}$  thick mylar film that could be continuously advanced past the vacuum side of the window minimally affects the laser beam quality, and, if refreshed every  $5 \times 10^4$  laser pulses, does not lead to loss of laser power. A reel-to-reel system for moving fresh film is commercially available.

The second engineering issue requiring attention is the development of a means for rapidly replacing the target material. The power densities and high-pulse rates used in our scoping studies rapidly damage the ablation target surface. After more than 20 pulses strike a single area, we begin to see evidence for the ejection of macroparticles which in most cases are not desired on the finished coating. In practical terms, this means that with a 300  $\mu\text{m}$  diameter laser spot on the target, we damage approximately one linear inch of one-inch diameter rod every  $3.5 \times 10^5$  shots (or every 80 seconds). The development of hardware to introduce virgin target material through a vacuum load locking system appears to be straightforward.

Similarly, at our projected deposition rates, a method for moving the substrate relative to the target to produce uniform coatings and a method to rapidly change out substrates will be required for a continuous production process. The requirement for short substrate change out time may be alleviated by multiplexing one laser source to several deposition chambers, potentially through optical fibers. Optical fibers may also allow development of a robotic structure that could deposit material inside large structures, either contained in a vacuum chamber or with its own vacuum system.

## **SUMMARY**

A promising pulsed laser deposition technology utilizing visible light has been demonstrated. Trial runs producing diamond-like-carbon have been encouraging. This technology appears to have significant advantages over other methods in deposition rate and surface morphology. More work is required to understand the physical characteristics of these coatings to verify their utility. Several proposed uses of DLC, or crystalline diamond films are: (1) low work function emitters for flat panel displays, (2) hard low-friction coatings for machine tool bits or infrared optics, and (3) corrosion resistant coatings for chemical processing systems. High rate pulsed laser deposition enables the economic application of numerous high value thin films.

## ACKNOWLEDGEMENTS

We wish to thank LLNL scientific staff W. J. Siekhaus and M. Balooch for the AFM measurements (Fig. 5) as well as M. A. Schildbach and G. A. Meyer for the EELS measurements (Figs. 2 ). We also wish to thank Louis Bernandez at Sandia National Laboratory, California, for the measurement of Raman spectra (Fig. 3). G. Huete, J. Poulter, and M. Solarski provided excellent support in the laboratory. R. Paris and J. Sullivan were instrumental in helping with electrical control aspects of the experiments. M. Havstad has helped identify engineering issues and is working to upgrade our hardware.

Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

## REFERENCES

1. (a) Mat. Res. Soc. Symp. Proc., Vol 191, Ed. by D.C. Paine and J.C. Bravman, 1990, Pg. 3, 129, 141, 147, 153, 159, 165, 171, 183, 199, 205, 211, 217. (b) Mat. Res. Soc. Symp. Proc., Vol 285, Ed. by B. Baren, J.J. Dubowski, and D.P. Norton, 1993, Pg. 15, 27, 33, 51, 263, 269, 281, 293, 299, 305, 311.
2. (a) Mat. Res. Soc. Symp. Proc., Vol 191, Ed. by D.C. Paine and J.C. Bravman, 1990, Pg. 25, 31. (b) Mat. Res. Soc. Symp. Proc., Vol 285, Ed. by B. Baren, J.J. Dubowski, and D.P. Norton, 1993, Pg. 87.
3. (a) C.B. Collins et al., Appl. Phys. Lett. 54 (1989), 216. (b) Mat. Res. Soc. Symp. Proc., Vol 285, Ed. by B. Baren, J.J. Dubowski and D.P. Norton, 1993, Pg. 215, 447, 547, 557.
4. Mat. Res. Soc. Symp. Proc., Vol 285, Ed. by B. Baren, J.J. Dubowski and D.P. Norton, 1993, Pg. 27, 39, 117, 507, 513.
5. (a) Mat. Res. Soc. Symp. Proc., Vol 191, Ed. by D.C. Paine and J.C. Bravman, 1990, Pg. 19, 43. (b) Mat. Res. Soc. Symp. Proc., Vol 285, Ed. by B. Baren, J.J. Dubowski and D.P. Norton, 1993, Pg. 263, 355.
6. C.M. Cotell et al, Patent Pending, Docket No. N.C., 73, 252.
7. S. Amirhagi et al., Mat. Res. Soc. Symp. Proc., 285 (1993), 489.
8. P.T. Murray and D.J. Peeler, J. Elec. Materials (submitted).
9. H.C. Tsai and D.B. Bogy, J. Vac. Sci. Technol. 5 (1987), 3287.
10. K. Saijo et al., Mater. and Manuf. Proc., 8 (1993), 59.
11. X. Chen and J. Narayan, Mat. Res. Soc. Symp. Proc., 286 (1993), 391.
12. C. D. Boley, "Computational Model of Drilling with High Radiance Pulsed Lasers," ICALEO (1994).





*Technical Information Department • Lawrence Livermore National Laboratory*  
University of California • Livermore, California 94551

